# PATENT ABSTRACTS OF JAPAN

(11)Publication number:

06-148889

(43)Date of publication of application: 27.05.1994

(51)Int.Cl.

GO3F 7/039

GO3F 7/004

GO3F 7/038

H01L 21/027

(21)Application number : 04-303512

(71)Applicant : FUJI PHOTO FILM CO LTD

(22)Date of filing:

13.11.1992

(72)Inventor: KONDO SHUNICHI

AOTANI NORIMASA UMEHARA AKIRA

(54) POSITIVE TYPE PHOTOSENSITIVE COMPOSITION

$$R_1 = 0$$

$$R_2 = C$$

$$R_3$$

(57)Abstract:

PURPOSE: To provide a positive type photosensitive compsn. having high photosensitivity and usable under light within a wide wavelength range.

CONSTITUTION: This positive type photosensitive compsn. contains a compd. (a) having at least two enol ether groups represented by the formula, a linear polymer (b) having an acid component and hydroxyl groups and a compd. (c) which is decomposed and generates an acid when irradiated with active light or radiation and the components (a) (b) are crosslinked with heat. In the formula each of R1-R3 is H, alkyl or aryl and two of them

may bond to each other to form a satd. or olefinic unsatd. ring.

#### **LEGAL STATUS**

[Date of request for examination]

15.11.1999

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

3206989

[Date of registration]

06.07.2001

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

#### \* NOTICES \*

JPO and INPIT are not responsible for any damages caused by the use of this translation.

- 1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

#### **CLAIMS**

#### [Claim(s)]

[Claim 1] (a) The compound and (b) which have at least two enol ether groups shown by the following general formula (I) The linear macromolecule which has an acid component and a hydroxyl group, and (c) Positive type photosensitivity constituent characterized by having contained the compound which decomposes by the exposure of an activity beam of light or a radiation, and generates an acid, and making the (a) component and the (b) component construct a bridge with heat.

#### [Formula 1]

$$R_1 = C = C \qquad (1)$$

$$R_2 = R_3 \qquad (1)$$

the inside of a formula, R1, and R2 And R3 hydrogen, an alkyl group, or an aryl group is expressed, and the same — or you may differ. Moreover, two of them may join together and the ring of saturation or olefin nature partial saturation may be formed.

#### **DETAILED DESCRIPTION**

[Detailed Description of the Invention]

#### [0001]

[Industrial Application] This invention relates to the positive type photosensitivity constituent which can form the lithography version, the proof of process printing, the drawing for over head projectors, and a resist pattern detailed in case the integrated circuit of a semiconductor device is manufactured further.

#### [0002]

[Description of the Prior Art] In the application of the lithography version etc., as the so-called photosensitive matter which is solubilized with an activity beam of light and which acts positively, the orthoquinone diazido compound is known conventionally and it is actually widely used for the lithography version etc. Such an orthoguinone diazido compound For example, U.S. Pat. No. 2,766,118, said -- the 2,767,092nd a number and 2,772,972 -- said -- the 2,859,112nd a number -- said -- the 2,907,665th a number -said -- the 3,046,110th a number and 3,046,111 -- said -- the 3,046,115th a number -- said -- the 3,046,118th a number -- said -- the 3,046,119th a number -- 3,046,120 -- said -- the 3,046,121st a number -- said -- the 3,046,122nd a number -- said -the 3,046,123rd a number and 3,061,430 -- said -- the 3,102,809th a number -- said -- the 3,106,465th a number -- said -- the 3,635,709th Each specification of a number and 3,647,443 is begun and it is indicated by many publications. Although it used that these orthoguinone diazido compounds caused decomposition by the exposure of an activity beam of light, produced the carboxylic acid of a five-membered ring, and served as alkali fusibility, it was not that all indicate sufficient sensibility to be. This originates in the quantum efficiency not exceeding 1 that it is difficult to carry out sensitization of the orthoquinone diazido compound in photochemistry, and in essence. Moreover, although the lithography version using these compounds etc. was produced by exposing in the shape of a pattern by a printer etc., and removing the exposure section with an alkali developer or a solvent, it tended to be influenced of the concentration of a developer and a solvent, temperature, and developing time, and it usually had the problem (development latitude is narrow) of sensibility changing. Moreover, since sensitization wavelength is fixed, light source fitness is scarce and white-light safety grant etc. is difficult, and it is Deep UV further. Since absorption in a field is large, it is not suitable for the application aiming at the improvement in resolution of the photoresist by low wavelength light use. Although the approach of a publication is tried by each official report and specifications, such as JP,48−12242,B, JP,52−40125,A, and U.S. Pat. No. 4,307,173, in order to conquer these faults for example, it has stopped at amelioration with insufficient all. [0003] Recently, some proposals are made for the purpose of development of the new positive type photosensitivity ingredient replaced with an orthoquinone diazido compound. As one of them, the polymer compound which has the alt.carbinol ester group indicated by JP,56-2696,B is mentioned. However, sensibility sufficient also in this case was not obtained. Although the approach of on the other hand creating using a photoresist as a pattern formation method for manufacturing electronic parts, such as a semiconductor device, magnetic bubble memory, and an integrated circuit, is generally performed The line breadth and spacing of a pattern become very small with densification, such as a semiconductor device, and high integration. Moreover, since dry etching came to be adopted as etching of a substrate, a photoresist comes to be expected high resolution and high dry etching resistance, and the mainstream of these photoresists is changing to the positive type from the negative mold. the positive type photoresist of the alkali development mold which used as the base the novolak resin of the alkali fusibility indicated by JIE C SUTORIETA work, KODAKKU microelectronics seminar proceedings, the 116th page (1976), etc., for example from excelling in sensibility, resolving power, and dry etching resistance also in a positive type photoresist especially -- current -- it is used widely. However, with diversification of electronic equipment, and high-sensitivity-izing, detailed-ization of a pattern is strongly demanded in recent years in order to attain high density and high integration further. The sensitization object which combined silicon polymers, such as a polysiloxane which gave alkali fusibility to the conventional orthoguinone diazido sensitization object, or poly sill methylene, to these demands, for example, JP,61-256347,A -- said -- 61-144639 a number -- said -- 62-159141 a number -said -- 62-191849 a number -- said -- 62-220949 a number -- said -- 62-229136 a photosensitive constituent given in each official report, such as a number, 63-90534, and 63-91654, -- The photosensitive constituent which combined the onium salt of an effective dose with the block copolymer of a polysiloxane/carbonate given in JP,62-136638,A is indicated. However, the manufacture became it is remarkable and difficult for functional grant of alkali fusibility etc., and the stability with the passage of time of these silicone polymers was not enough, either. [0004] Moreover, the compound from which hydrolysis etc. is produced with the compound and acid which generate an acid by light as a sensitive material of the positive type which replaces quinone diazide conventional recently, and the solubility to the alkaline water changes, and the constituent which contains binder resin etc. if needed are reported. For example, the approach of decomposing O, N-acetal (U.S. Pat. No. 3,779,778), the ortho ester, and the amide acetal (the 2610842nd number of the West Germany country patent public presentation official report) which contain an aromatic compound as the acetal and hydroxyl, or amine component of specific low molecular weight or the amount of macromolecules, and making a positive image forming with the acid generated in exposure can be mentioned. Furthermore, the method of making a positive image form by the same approach JP,64-33546,A -- said -- No. 89003 [ 48 to ] -- said -- the 51-120714th a number -- said -- the

53–133429th a number — said — the 55–126236th a number — said — the 53–133428th a number — said — No. 12995 [ 55 to ] — said — No. 31674 [ 57 to ] — said — No. 31675 [ 57 to ] — said — No. 37347 [ 57 to ] — said — the 62–215947th It is indicated by a number, JP,1–106040,A, and JP,1–106041,A. However, each of these constituents has low sensibility, its difference of the solubility of an unexposed part and the exposure section is small, or a problem is in the configuration of the pattern of a positive image, and by the time practical use is presented, they will not have resulted. Moreover, it is indicated by JP,62–45971,A as an acidolysis nature compound using the compound containing an enol ether group that a positive image can be formed by the same approach. However, also in this case, since the difference of the solubility of an unexposed part and the exposure section was small, the clear positive image was able to be obtained only on the limited conditions low [ sensibility ]. [0005]

[Problem(s) to be Solved by the Invention] The purpose of this invention is to offer the new positive type photosensitivity constituent for solving the above-mentioned trouble. That is, it is in having high photosensitivity and offering the new positive type photosensitivity constituent in which use with a wide range wavelength light is possible. The soluble difference of the exposure section and an unexposed part of the purpose of the further this invention is large, and is to offer a positive type photosensitivity constituent with high development latitude.

#### [0006]

[Means for Solving the Problem] The compound which contains enol ether groups, such as two or more vinyl ether radicals, as a result of looking for the new positive type photosensitivity constituent which replaces orthoquinone diazido that this invention person should attain the above-mentioned purpose, For example, the thing which the above-mentioned component carries out heat bridge formation effectively with desiccation heat, and is become insoluble at an alkali water solution, a solvent, etc. when dilution preparation of the hydroxyl-group content acrylic resin is carried out with a solvent and spreading desiccation is carried out on a base material, Furthermore, this heat bridge formation section finds out hydrolyzing efficiently and solubilizing by acid's existence-ization, and came to complete this invention. That is, this invention is (a). The compound which has at least two enol ether groups shown by the following general formula (I), (b) The linear macromolecule which has an acid component and a hydroxyl group, and the compound which decomposes by the exposure of (c) activity beam of light or a radiation, and generates an acid are contained. (a) A component and (b) It is the positive type photosensitivity constituent

characterized by making a component construct a bridge with heat, and to ultraviolet rays, a visible ray, an electron ray, or an X-ray, high photosensitivity is shown and it is related with the photosensitive constituent which can form a clear positive image on large development conditions.

#### [0007]

[Formula 2]

$$R_{1}$$
  $C = C$   $R_{2}$  (1)

[0008] the inside of a formula, R1, and R2 And R3 hydrogen, an alkyl group, or an aryl group is expressed, and the same — or you may differ. Moreover, two of them may join together and the ring of saturation or olefin nature partial saturation may be formed. Hereafter, this invention is explained to a detail.

[0009] Although this invention has the positive type photosensitivity constituent which consists of three components of the above (a), (b), and (c), the first description is for the enol ether group content compound of a component (a) and the linear macromolecule of a component (b) to make the structure of cross linkage thermally. First, the enol ether group content compound of the component (a) of this invention is explained. It sets to the enol ether group of a general formula (I), and is R1 and R2. And R3 When it is an aryl group, generally it has 4-20 carbon atoms, and an alkyl group. an aryl group, an alkoxy group, an aryloxy group, an acyl group, an acyloxy radical, an alkyl sulfhydryl group, an aminoacyl radical, a carboalkoxy radical, the nitro group, the sulfonyl group, the cyano group, or the halogen atom may permute. R1 and R2 And R3 When it expresses an alkyl group, the alkyl group of the straight chain of the saturation of carbon numbers 1-20 or partial saturation, branching, or alicycle is shown, and a halogen atom, a cyano group, an ester group, the oxy-radical, the alkoxy group, the aryloxy group, or the aryl group may permute. R1 and R2 And R3 the case where any two join together and a cycloalkyl radical or a cyclo alkenyl radical is formed -- usually -- 3-8 -- 5 or six ring members are expressed preferably. [ moreover, ] The desirable thing among the enol ether groups shown by the general formula (I) in this invention is R1 and R2. And R3 The enol ether group whose one is a methyl group or an ethyl group inside and whose remainder is a hydrogen atom, and a still more desirable thing are R1 and R2. And all R3 is the vinyl ether radical which is hydrogen. Although the various compounds containing two or more enol ether groups can be used in this invention, these are compounds which have the boiling point 60 degrees C or more

under atmospheric pressure, and the following general formula (II) or (III) the shown vinyl ether compound is mentioned as a compound with a desirable component (a). [0010]

[Formula 3]

$$A - \left[ -O - (R_4 - O)_n - CH = CH_2 \right]_m$$
 (11)

$$A - \left[ -B - R_4 - O - CH = CH_2 \right]_m \tag{111}$$

[0011] here -- A -- the alkyl group, aryl group, or heterocycle radical of m \*\* -- being shown -- B -CO-O- and -NHCOO- or -- -NHCONH- being shown -- R4 The straight chain of carbon numbers 1-10 or the alkylene group of branching is shown, n shows the integer of 0, or 1-10, and m shows the integer of 2-6. The compound shown by the general formula (II) is for example, Stephen.C.Lapin, Polymers Paint Colour Journal, 179 (4237), and 321 (1988). It is compoundable with the reaction of the reaction of the approach indicated, i.e., polyhydric alcohol, a polyhydric phenol, and acetylene, polyhydric alcohol or a polyhydric phenol, and alkyl halide vinyl ether. As an example, the ethylene glycol divinyl ether, triethylene glycol divinyl ether, The 1,3-butanediol divinyl ether, the tetramethylene glycol divinyl ether, The neopentyl glycol divinyl ether, the trimethylol propane TORIBI nil ether, The trimethylolethane TORIBI nil ether, the hexandiol divinyl ether, 1, 4-cyclohexane diol divinyl ether, tetraethylene glycol divinyl ether, The pentaerythritol divinyl ether, the pentaerythritol TORIBI nil ether, The pentaerythritol tetravinyl ether, the sorbitol tetravinyl ether. SORUBIRUPENTA vinyl ether, ethylene glycol diethylene vinyl ether, Triethylene glycol diethylene vinyl ether, ethylene glycol JIPURO pyrene vinyl ether, Triethylene glycol diethylene vinyl ether, trimethylol propane TORIECHIREN vinyl ether, Trimethylol propane diethylene vinyl ether, pentaerythritol diethylene vinyl ether, Pentaerythritol TORIECHIREN vinyl ether, pentaerythritol tetra-ethylene vinyl ether, Although 1, 2-JI (vinyl ether methoxy) benzene, 1, 2-JI (vinyl ether ethoxy) benzene, and the compound shown in a list by the following general formula (II-1) - (II-41) can be mentioned, it is not limited to this.

## [0012]

## [Formula 4]

$$CH_{z} = CH - O - CH_{z}CH_{z}O$$

$$OCH_{z}CH_{z}O - CH = CH_{z}$$

$$CH_2 = CH - O - CH_2 CH_1 O - CH = CH_2$$

### [0013]

### [Formula 5]

$$CH_z = CH - OCH_zCH_zO - OCH_zCH_zO - CH = CH_z$$

$$(H_2 = CH - O - CH_2CH_2 - O - CH_2CH_2O - CH = CH_2CH_2O - CH_2CH_2O - CH = CH_2CH_2O - CH_2$$

$$(11-8)$$
 $CH_z = CH - O - CH_z - CH_z - O$ 
 $OCH_zCH_zO - CH = CH_z$ 
 $CH_z$ 

$$(II - 9)$$
 $CH_z = CH - 0 - CH_z CH_z O - CH = CH_z$ 
 $OCH_z CH_z - 0 - CH = CH_z$ 
 $OCH_z CH_z - 0 - CH = CH_z$ 

## [0014]

[Formula 6]

$$CH_{2}=CH-O-CH_{2}O$$
 $CH_{3}=CH-O-CH_{2}O$ 
 $CH_{4}=CH_{3}O$ 
 $CH_{4}=CH_{4}O$ 
 $CH_{5}=CH_{5}O$ 
 $CH_{5}=CH_{$ 

## [0015]

## [Formula 7]

$$CH_{z} = CH - O - CH = CH$$

$$CH_2 = CH - 0$$
 $CH_2 = CH - 0$ 
 $CH_3 = CH - 0$ 
 $CH_3 = CH - 0$ 
 $CH_3 = CH - 0$ 

$$CH_{z} = CH - 0$$
  $OCH = CH_{z}$ 

## [0016]

[Formula 8]

$$(11-20)$$

$$-20$$
)
 $CH_{2} = CH - 0$ 
 $S - CH = CH_{2}$ 

$$CH_{1} = CH - O$$

$$CH_{2} = CH - O$$

$$CH_{3} = CH - O$$

$$CH_{3} = CH - O$$

$$CH_{4} = CH_{2}$$

$$CH_{1} = CH - 0$$
 $CF_{1}$ 
 $CF_{2}$ 
 $CF_{3}$ 
 $CF_{3}$ 

$$CH_{z} = CH$$

$$OCH = CH_{z}$$

$$OCH = CH_{z}$$

# [0017]

# [Formula 9]

$$(-11-24)$$

$$CH_2 = CH_2$$
 $CH_3 = CH_3$ 
 $CH_4 = CH_3$ 
 $CH_4 = CH_3$ 

$$(11 - 25)$$

$$CH_{2} = CH_{2}$$

$$CH_{3} = CH_{2}$$

$$CH_{3} = CH_{2}$$

# [0018]

## [Formula 10]

$$(-11-26)$$

$$CH_{2} = CH_{2}$$

$$CH_{2} = CH_{2}$$

$$CH = CH_{2}$$

$$CH = CH_{2}$$

## [0019]

# [Formula 11]

$$CH_{7} = CH - O$$

$$CH_{3}$$

$$C$$

$$CH_2 = CH - 0$$

$$0 - CH = CH_2$$

# [0020]

## [Formula 12]

$$CH_{2} = CH - O$$

$$CH = CH_{2}$$

$$CH = CH_{3}$$

$$CH = CH_{4}$$

$$COMe$$

$$OCH = CH_{2}$$

$$OCH = CH_{3}$$

$$(11-31)$$

$$CH_2 = CH - 0$$

$$Me$$

$$OCH = CH_2$$

$$Me$$

$$OCH = CH_2$$

$$Me$$

$$Me$$

## [0021]

# [Formula 13]

$$CH_2 = HCO$$

$$OCH = CH_2$$

$$OCH = CH_2$$

$$CH_{2} = HC$$

$$OCH = CH_{2}$$

$$CH_{2} = CHO$$

$$Me$$

$$Me$$

$$OCH = CH_{2}$$

$$OCH = CH_{2}$$

# [0022]

## [Formula 14]

(11-34)

$$CH_2 = CH_2$$
 $Me$ 
 $M$ 

$$(11-35)$$

$$CH_{z} = CH_{0}$$

$$CH_{z} = CH_{0}$$

$$CH_{z} = CH_{0}$$

$$CH_{z} = CH_{0}$$

$$CH_{z} = CH_{z}$$

$$CH_2 = CH - 0$$
  $OCH = CH_2$   $CH_2 = CH - 0$   $OCH = CH_2$ 

## [0023]

### [Formula 15]

$$CH_{z} = CH - 0$$

$$CH_{z} = CH - 0$$

$$Me$$

$$Me$$

$$O - CH = CH_{z}$$

$$CH_{z} = CH - 0$$

$$Me$$

$$Me$$

$$CH_{2} = CH - O$$

OCH = CH<sub>2</sub>

$$CH_2 = CHO$$

$$CH_2 = CH$$

$$OCH = CH_2$$

#### [0024]

#### [Formula 16]

$$(11-40)$$

$$CH_{2} = CH - 0$$
 $OCH = CH_{2}$ 
 $OCH = CH_{2}$ 

$$CH_{2} = CH - 0$$

$$CH_{2} = CH - 0$$

$$CH_{3} = CH - 0$$

$$CH_{4} = CH_{5}$$

$$CH_{4} = CH_{5}$$

$$CH_{5} = CH_{5}$$

$$CH_{6} = CH_{7}$$

$$CH_{7} = CH_{7}$$

$$CH_{1} = CH_{2}$$

$$CH_{2} = CH_{3}$$

$$CH_{3} = CH_{4}$$

$$CH_{4} = CH_{5}$$

$$CH_{5} = CH_{5}$$

$$CH_{6} = CH_{7}$$

$$CH_{7} = C$$

[0025] On the other hand, the compound shown by the general formula (III) (in the case of B=CO-O-) can be manufactured by the reaction of polyvalent carboxylic acid and alkyl halide vinyl ether. Although terephthalic-acid diethylene vinyl ether, phthalic-acid diethylene vinyl ether, isophthalic acid diethylene vinyl ether, phthalic-acid Zypro pyrene vinyl ether, terephthalic-acid Zypro pyrene vinyl ether, isophthalic acid Zypro pyrene vinyl ether, maleic-acid diethylene vinyl ether, fumaric-acid diethylene vinyl ether, itaconic-acid diethylene vinyl ether, etc. can be mentioned as an example, it is not limited to these. Furthermore, the vinyl ether radical content compound compounded by the reaction of the vinyl ether compound which has active hydrogen shown by the following general formula (IV), (V), or (VI) as a vinyl ether radical content compound suitably used in this invention, and the compound which has an isocyanate radical can be mentioned.

[0026]

$$CH_2 = CH - O - R^2 - OH$$
 (TV)

$$CH_2 = CH - O - R^1 - COOH \qquad (7)$$

$$CH2 = CH - O - R' - NH2$$
 (TT)

[0027] Here, it is R1. The straight chain of carbon numbers 1–10 or the alkylene group of branching is shown. As a compound containing an isocyanate radical, the compound of a publication can be used for a cross linking agent handbook (the TAISEI CORP. \*\*, 1981 issue), for example. Specifically Triphenylmethane color triisocyanate, diphenylmethane diisocyanate, Tolylene diisocyanate, 2, the dimer of 4–tolylene diisocyanate, Naphthalene –1, 5–diisocyanate, o–tolylene diisocyanate, Polyisocyanate molds, such as polymethylene polyphenyl isocyanate and hexamethylene diisocyanate, Polyisocyanate adduct molds, such as an adduct of tolylene diisocyanate, the adduct of trimethylol propane and hexamethylene diisocyanate, and water and an adduct of xylene diisocyanate and trimethylol propane, etc. can be mentioned.

[0028] The various compounds which have a vinyl ether radical in an end are made by making the above-mentioned isocyanate radical content compound and an active hydrogen content vinyl ether compound react. Although the examples of a compound with the vinyl ether radical used for this invention below are enumerated, the range of this invention is not limited to these.

### [0029]

[Formula 18]

(知 - 2)
CH<sub>z</sub> = CHOCH<sub>z</sub>CH<sub>z</sub>OOC - NH NH - COO - CH<sub>z</sub>CH<sub>z</sub>OCH = CH<sub>z</sub>

### [0030]

[Formula 19]

$$CH_{2} = CHOCH_{2}CH_{2}NH - C - NH - C - NHCH_{2}CH_{2}OCH = CH_{2}$$

$$0$$

$$0$$

$$0$$

### [0031]

[Formula 20]

$$(OII - 10)$$

### [0032]

[Formula 21]

[0033] Although the compound containing at least two vinyl ether radicals described above is single and it can be used, you may use it as several sorts of mixture. Generally the addition of the compound containing the vinyl ether radical in a photosensitive constituent is 5 - 50% of the weight of the range preferably one to 80% of the weight to the total solids of a photosensitive constituent. The linear macromolecule (b) which has a part for acidity and the hydroxyl group which are used by this invention constructs a bridge thermally with the compound (a) which has at least two enol ether groups, and if the bridge formation section decomposes efficiently with an acid, it can be chosen and used for arbitration. Although the above-mentioned linear macromolecule is compoundable by the well-known method of generally obtaining a linear macromolecule, it can obtain by, for example, copolymerizing a part for acidity, the vinyl monomer which has a carboxylic-acid radical, a sulfonic group, a phosphoric-acid radical, a sulfonamide radical, etc. preferably, and the vinyl monomer which has a hydroxyl group. Copolymerization of the vinyl monomer of further others may be carried out if needed. As a vinyl monomer containing a part for acidity, an acrylic acid, a methacrylic acid, a maleic acid, an itaconic acid, a crotonic acid, isocrotonic acid, p-vinyl benzoic acid, p-vinylbenzene sulfonic acid, p-vinyl cinnamic acid, the maleic-acid monomethyl ether, the maleic-acid monoethyl ether, etc. are mentioned, for example. [0034] As a vinyl monomer containing a hydroxyl group, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, p-2-hydroxyethyl styrene, N-(2-hydroxyethyl) maleimide, p-hydroxystyrene, N-(4-hydroxyphenyl) methacrylamide, etc. are mentioned, for example. As the above-mentioned monomer and other copolymerizable monomers For example, acrylonitrile, acrylamide, methacrylamide, methyl acrylate, Ethyl acrylate, propylacrylate, butyl acrylate, Methyl methacrylate, ethyl methacrylate, propyl methacrylate, Butyl methacrylate, styrene, benzyl acrylate, benzyl methacrylate, Vinyl benzoate, a vinyl chloride, vinylidene chloride, vinyl acetate, N-(4-sulfamoyl phenyl) methacrylamide, N-phenyl phosphonyl methacrylamide, a butadiene, a chloroprene, IMEPUREN, etc. can be mentioned. As a desirable copolymerization ratio of the vinyl monomer containing a part for acidity, the vinyl monomer containing a hydroxyl group, and other copolymerizable monomers, it is weight % and is the range of 5-80:2-80:0-97.

[0035] Although these linear macromolecules are single and it can be used, you may use it as several sorts of mixture. Generally the addition of the linear macromolecule in a photosensitive constituent is 20 - 90% of the weight of the range preferably one to 95% of the weight to the total solids of a photosensitive constituent, the molecular

weight of a linear macromolecule — general — 1,000–1,000,000 — desirable — 1,500–200,000 it is. Moreover, although what has an acid component and a hydroxyl group in one linear—macromolecule chain as mentioned above is desirable as a linear macromolecule used for this invention, in a specific development solvent, it can also obtain in the mixture of the linear macromolecule which has an acid component for the same effectiveness, and the linear macromolecule which has a hydroxyl group. The compounds which generate an acid by the well–known light currently used for the photoinitiator of optical cationic polymerization, the photoinitiator of an optical radical polymerization, the optical decolorizing agent of coloring matter, optical alterant, or a micro resist as a compound which decomposes by the exposure of the activity beam of light or radiation used by this invention, and generates an acid, and those mixture can be used choosing them suitably.

[0036] For example S.I.Schlesinger, Photogr.Sci.Eng., 18, and 387 (1974), T.S.Bal et al, Polymer, 21, and 423 (1980) etc. — the diazonium salt of a publication — U.S. Pat. No. 4,069,055 -- said -- 4,069,056 A number and \*\* the specification of Re No. 27,992 --Ammonium salt given in the specification of Japanese Patent Application No. No. 140140 [ three to ] etc., D.C.Necker et al, Macromolecules, 17, 2468 (1984), C.S.Wen et al, Teh, Proc.Conf.Rad.Curing ASIA, p478 Tokyo, and Oct (1988), U.S. Pat. No. 4,069,055 -- said -- 4,069,056 phosphonium salt given in specifications, such as a number, -- J.V.Crivello et al, Macromorecules, 10 (6), 1307 (1977), Chem.& Eng.News, Nov.28, and p31 (1988), Europe patent 104,143rd a number and U.S. Pat. No. 339,049 -- said -- the 410,201st a number -- Iodonium salt given in a specification or an official report of JP,2-150848,A and JP,2-296514,A etc., J.V.Crivello et al, Polymer J.17, and 73 (1985), J.V.Crivello et al.J.Org.Chem., 43, and 3055 (1978), W.R.Watt etal, J.Polymer Sci., Polymer Chem.Ed., 22, and 1789 (1984), J.V.Crivelloet al, Polymer Bull., 14, and 279 (1985), J.V.Crivello et al, Macromorecules, and 14 (5) 1141 (1981), J.V.Crivello et al, J.Polymer Sci., PolymerChem.Ed., 17, and 2877 (1979), Europe patent 370,693rd Number, said -- 3,902,114 a number -- said -- 233,567 a number -said -- 297,443 a number -- said -- 297,442 a number and U.S. Pat. No. 4,933,377 -said -- No. 161,811 -- said -- 410,201 a number -- said -- 339,049 a number -- said -- 4,760,013 a number -- said -- 4,734,444 a number -- said -- 2,833,827 A number and Germany patent 2,904,626th a number -- said -- 3,604,580 a number -- said --3,604,581 Sulfonium salt given in a specification or an official report of a number etc., and [0037] J. V.Crivello et al, Macromorecules, 10 (6), 1307 (1977), J.V.Crivello et al, J.Polymer Sci., Polymer Chem.Ed., 17, and 1047 (1979) etc. -- the seleno NIUMU salt of a publication -- Onium salt, such as arsonium salt given (1988) in C.S.Wen et al,

Teh, Proc.Conf.Rad.Curing ASIA, p478Tokyo, Oct, etc., U.S. Pat. No. 3,905,815, JP,46–4605,B, JP,48–36281,A, JP,55–32070,A, JP,60–239736,A, JP,61–169835,A, JP,61–169837,A, JP,62–58241,A, JP,62–212401,A, An organic halogenated compound given in a specification or an official report of JP,63–70243,A and JP,63–298339,A etc., K.Meier et al, J.Rad.Curing, 13 (4), 26 (1986), T.P.Gill et al, Inorg.Chem., 19, and 3007 (1980), D.Astruc, Acc.Chem.Res., 19 (12), An organic metal / organic halogenide given in 377 (1896), JP,2–161445,A, etc., S.Hayase et al, J.Polymer Sci., 25, and 753 (1987), E.Reichmanis et al, J.Polymer Sci., Polymer Chem.Ed., 23, and 1 (1985), Q.Q.Zhu et al, J.Photochem., 36, 85, 39, 317 (1987), B.Amit et al, and Tetrahedron Lett., (24) 2205 (1973).

[0038] D. H.R.Barton et al, J.Chem Soc., and 3571 (1965), P.M.Collins et al, J.Chem.Soc., Perkin I, and 1695 (1975), M.Rudinstein et al and TetrahedronLett., (17), 1445 (1975), J.W.Walker et al, J.Am.Chem.Soc., 110, and 7170 (1988), S.C.Busman et al, J.Imaging Technol., 11 (4), 191 (1985), H.M.Houlihan et al, Macoromolecules, 21, and 2001 (1988), P.M.Collinset al, J.Chem.Soc., Chem.Commun., and 532 (1972), S.Hayase et al, Macromolecules, 18, and 1799 (1985), E.Reichmanis et al, J.Electrochem.Soc., Solid State Sci. Technol., 130 (6), F.M. Houlihan et al, Macromolecules, 21, and 2001 (1988), the Europe patent 0290th and No. 750 -- said -- 046 and 083 a number -said -- 156 and 535 a number -- said -- 271,851 a number -- said -- 0,388,343 a number and U.S. Pat. No. 3,901,710 -- said -- 4,181,531 the photo-oxide generating agent which has o-nitrobenzyl mold protective group of a publication in a specification or an official report of a number, JP,60-198538,A, and JP,53-133022,A etc. --M.TUNOOKA et al, Polymer Preprints Japan, 38 (8), G.Berner et al, J.Rad.Curing, 13 (4), W.J.Mijs et al, Coating Technol., 55 (697), 45 (1983), Akzo, H.Adachi et al, Polymer Preprints, Japan, 37 (3), the Europe patent 0199th and No. 672 -- said -- 84515 a number -- said -- 199 and 672 a number -- said -- 044 and 115 a number -- said --No. 0101 or 122 and U.S. Pat. No. 4,618,564 -- said -- 4,371,605 a number -- said --4,431,774 a number and JP,64-18143,A -- A disulfon compound given in the compound which photodissociates and generates a sulfonic acid and JP,61-166544,A which are represented by imino sulfonate given in JP,2-245756,A, the official report of Japanese Patent Application No. No. 140109 [ three to ], or a specification etc. can be mentioned.

[0039] Moreover, the radical which generates an acid by such light or the compound which introduced the compound into the principal chain or side chain of a polymer, For example, M.E.Woodhouse et al, J.Am.Chem.Soc., 104, and 5586 (1982), S.P.Pappas et al, J.Imaging Sci., 30 (5), 218 (1986), S.Kondo er al.Makromol.Chem., Rapid Commun.,

and 9,625 (1988), Y.Yamada et al, Makromol.Chem., 152, 153, and 163 (1972), J.V.Crivello er al.J.Polymer Sci., Polymer Chem.Ed., 17, and 3845 (1979), U.S. Pat. No. 3,849,137 and Germany patent 3,914,407th, JP,63-26653,A, JP,55-164824,A, JP,62-69263,A, The compound of a publication can be used for a specification or an official report of JP,63-1460387,A, JP,63-163452,A, JP,62-153853,A, and JP,63-146029,A etc.

[0040] Furthermore, V.N.R.Pillai and Synthesis, (1), 1 (1980), A.Abad et al, and Tetrahedr on Lett., (47) 4555 (1971), D.H.R.Barton et al and J.Chem.Soc., (C), 329 (1970), U.S. Pat. No. 3,779,778, and Europe patent 126,712nd The compound which generates an acid by the light of a publication can also be used for a number etc. In the compound which decomposes by the exposure of the above-mentioned activity beam of light or a radiation, and generates an acid, especially the thing used effectively is explained below.

(1) The following general formula which the trihalomethyl group permuted (VIII) The oxazole derivative or the following general formula (IX) expressed S-triazine derivative expressed.

[0041]

[Formula 22]

[0042]

[Formula 23]

$$Y_3C$$
 $N$ 
 $N$ 
 $CY_3$ 
 $CY_3$ 

[0043] The inside of a formula, and R1 It is the aryl group or alkenyl radical which is not permuted [ a permutation or ], and R2 is the aryl group which is not permuted [ a permutation or ], an alkenyl radical, an alkyl group, or -CY3. It expresses. Y shows a

chlorine atom or a bromine atom. The above-mentioned oxazole derivative (VIII) And S-triazine derivative (IX) As an example, although following VIII-1-8 and compound IX-1-10 can be mentioned, it is not limited to this.

[0044]

[Formula 24]

$$CH = CH - C C - CCI_3$$

$$N - N$$

$$N - N$$

$$N - N$$

$$n-C_4H_9O \longrightarrow CH=CH-C C C-CCI_3$$

$$\begin{array}{c} N-N \\ CH=CH-C \\ (VIII -5) \end{array}$$

[0045]

[Formula 25]

$$\begin{array}{c|c} & & & & & & & & & & \\ & & & & & & & \\ & & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & &$$

# [0046]

[Formula 26]

$$Cl_3$$
 $Cl_3$ 
 $Cl_3$ 
 $Cl_3$ 
 $CCl_3$ 
 $CCl_3$ 

# [0047]

# [Formula 27]

CI<sub>3</sub>C 
$$(\mathbb{K} - 4)$$

CI<sub>3</sub>C  $(\mathbb{K} - 4)$ 

OCH<sub>3</sub>

CI<sub>3</sub>C  $(\mathbb{K} - 5)$ 

OCH<sub>3</sub>

CI<sub>3</sub>C  $(\mathbb{K} - 6)$ 

## [0048]

## [Formula 28]

$$CI_{3}\dot{C} \qquad N \qquad CCI_{3}$$

$$CI_{3}\dot{C} \qquad N \qquad CCI_{3}$$

$$CH=CH \qquad N \qquad N \qquad CCI_{3}$$

$$CH=CH \qquad CH=CH \qquad CH=CH$$

$$CH=CH \qquad N \qquad N \qquad CCI_{3}$$

$$CI_{3}C \qquad N \qquad CCI_{3}$$

[0049] (2) Sulfonium salt expressed with the iodonium salt or the following general formula (XI) expressed with the following general formula (X).
[0050]

[Formula 29]

$$Ar^{1} \setminus I^{*} Z^{*} (X)$$

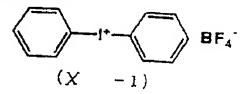
$$Ar^{2} \setminus I^{*} Z^{*} (X)$$

[0051] [Formula 30] R<sup>3</sup>

[0052] Ar1 and Ar2 show respectively the aryl group which is not permuted [ a permutation or ] independently among a formula. As a desirable substituent, an alkyl group, a halo alkyl group, a cycloalkyl radical, an aryl group, an alkoxy group, a nitro group, a carboxyl group, an alkoxy carbonyl group, a hydroxy group, a sulfhydryl group, and a halogen atom are mentioned. R3 and R4 And R5 The alkyl group or aryl group which is not permuted [ a permutation or ] is shown independently respectively. They are the aryl group of carbon numbers 6-14, the alkyl groups of carbon numbers 1-8, or those permutation derivatives preferably. A desirable substituent is the alkoxy group of carbon numbers 1-8, the alkyl group of carbon numbers 1-8, a nitro group, a carboxyl group, a hydroxy group, or a halogen atom to an aryl group, and are the alkoxy group of carbon 1-8, a carboxyl group, and an alkoxy carbonyl group to an alkyl group. Z- a \*\*\*\* anion -- being shown -- for example, -- Although condensation polykaryotic aromatic series sulfonic-acid anions, such as a BF4-, AsF6-, PF6-, SbF6-, SiF6-, CIO4-, CF3SO3-, BPh4-, and (Ph= phenyl) naphthalene-1-sulfonic-acid anion, an anthraquinone sulfonic-acid anion, a sulfonic group content color, etc. can be mentioned, it is not limited to these. [0053] Moreover, R3 and R4 And R5 Ar1 and Ar2 may be combined with inner 2 lists through single bond or a substituent, respectively. The above-mentioned onium salt shown by the general formula (X) and (XI) is well-known. For example, J.W.Knapczyk et al, J.Am.Chem.Soc., 91, and 145 (1969), A.L.Maycok et al, J.Org.Chem., 35, and 2532 (1970), E.Goethas etal, Bull.Soc.Chem.Belg., 73, and 546 (1964), H.M.Leicester, J.Am.Chem.Soc., 51, and 3587 (1929), J.B.Crivello etal, J.Polym.Chem.Ed., 18, and 2677 (1980), U.S. Pat. No. 2,807,648 — and — said — 4,247,473 It is compoundable by the approach of a publication in a specification or an official report of a number and JP,53-101,331,A etc. A general formula (X) and (XI) Although compound X-1-22 shown below and XI-1-34 are mentioned as an example of an onium compound, it is not limited to this.

# [0054]

## [Formula 31]



$$(X - 2)$$
  $PF_6$ 

$$(X - 3)$$
AsF<sub>6</sub>

$$(X -3)$$

$$(X -4)$$

$$SbF_6$$

## [0055]

$$(X - 6)$$
 OCH<sub>3</sub> PF<sub>6</sub>

$$(X - 7)$$

$$O_2N$$

$$(X -8) O_2N$$

$$(X - 9)$$

$$-NO_2 BF_4$$

## [0056]

[Formula 33]

$$H_3C$$
 $I^*$ 
 $CH_3$  AsF<sub>6</sub>

$$H_3C$$
  $(X$   $-1$   $1$   $CH_3$   $SbF_6$ 

$$n-C_7H_{15}$$
  $-1^+$   $-1^-C_7H_{15}$   $PF_6$ 

$$CI \longrightarrow I^{+} \longrightarrow CI \quad PF_{6}$$

# [0057]

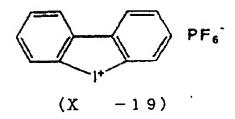
[Formula 34]

$$H_3COOC$$
 $(X -15)$ 
 $PF_6$ 
 $COOCH_3$ 

$$^{t}Bu$$
 $I^{+}$ 
 $^{t}Bu$ 
 $SbF_{6}^{-}$ 
 $(X - 17)$ 

# [0058]

[Formula 35]



$$(X -20)$$

# [0059]

[Formula 36]

(X - 2 2)

## [0060]

[Formula 37]

$$(X \mid -1)$$
S+ BF<sub>4</sub>

$$(X \mid -2)$$

$$S^{+} \quad PF_{6}$$

$$(x_1 - 3)$$
S+ AsF<sub>6</sub>

## [0061]

[Formula 38]

$$(XI - 4)$$
Start SbF<sub>6</sub>

$$(x_1 - 5)$$
S+ CF<sub>3</sub>SO<sub>3</sub>

$$H_3C$$
 $S^*$ 
 $OC_2H_5$ 
 $BF_4$ 

$$H_3CO - S^+ - CI$$
  $BF_4$ 

## [0062]

[Formula 39]

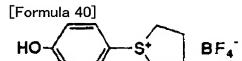
$$S^{+}$$
-CH<sub>2</sub>CI BF<sub>4</sub>  
CH<sub>3</sub>  
( $(X 1 - 8)$ 

HO
$$\begin{array}{c|c}
& S^{+}\text{-CH}_{3} & PF_{6} \\
& CH_{3} \\
& (X | -9)
\end{array}$$

$$H_3C$$
 $S^+-CH_3$ 
 $CH_3$ 
 $(XI-10)$ 

$$H_3C$$
 $S^+-CH_3$ 
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 

## [0063]



$$(XI-12)$$

$$H_3CO$$
 $H_3CO$ 
 $H_3C$ 

$$n-C_4H_9$$
 $HO-S^+$ 
 $PF_6$ 
 $n-C_4H_9$ 
 $(X/-14)$ 

HO-
$$S+$$
 BF<sub>4</sub>.

(XI-15)

## [0064]

[Formula 41]

## [0065]

[Formula 42]

$$\begin{array}{c|cccc}
O & & & & & \\
\hline
-C-CH_2-S^+-CH_3 & & SbF_6
\end{array}$$

$$\begin{array}{c|cccc}
CH_3 & & & & \\
\hline
(X|-19) & & & & \\
\end{array}$$

$$\begin{array}{c}
0 \\
1 \\
-C - CH_2 - S^{\bullet}
\end{array}$$
(XI - 21)

$$CI$$
 $CI$ 
 $(XI-22)$ 

AsF<sub>6</sub>

## [0066]

[Formula 43]

$$(X \mid -2 \mid 3)$$

$$C-CH_2-S+BF_4$$

$$(\times 1-24)$$

$$S \leftarrow S + \left( \begin{array}{c} \\ \\ \\ \\ \end{array} \right)_{2} PF_{6}$$

## [0067]

[Formula 44]

$$S+ \left( \begin{array}{c} \\ \\ \\ \\ \end{array} \right)_2 SbF_6$$

$$\left\{ \left( \begin{array}{c} \\ \\ \\ \\ \end{array} \right)_{2} S^{*} \left( \begin{array}{c} \\ \\ \\ \end{array} \right)_{2} S^{2} PF_{6} S^{2}$$

$$(\times) -30)$$

## [0068]

[Formula 45]

H<sub>3</sub>C 
$$\longrightarrow$$
 S<sup>+</sup>  $\longrightarrow$  OC<sub>2</sub>H<sub>5</sub>  $\bigcirc$  (XI - 3 1)

### [0069]

[Formula 46]

$$(X | -3 4)$$

[0070] (3) The imino sulfonate derivative expressed with the disulfon derivative or the following general formula (XIII) expressed with the following general formula (XII). [0071]

[Formula 47]

$$Ar^3-SO_2-SO_2-Ar^4$$
 $(XI)$ 

[0072]

[Formula 48]

[0073] Ar3 and Ar4 show respectively the aryl group which is not permuted [ a permutation or ] independently among a formula. R6 The alkyl group or aryl group which is not permuted [ a permutation or ] is expressed. A shows the alkylene group which is not permuted [ a permutation or ], an ARUKENIRUN radical, or an arylene radical. a general formula (XII) — and (XIII) Although compound XII—1—12 shown below and XIII—1—12 are mentioned as an example of the compound shown, it is not limited to this.

[0074]

[Formula 49]

$$CI \longrightarrow SO_2 - SO_2 \longrightarrow C$$

$$H_3C$$
  $SO_2$   $SO_2$   $CH_3$ 

$$H_3CO$$
 $SO_2$ 
 $SO_2$ 
 $OCH$ 

## [0075]

[Formula 50]

$$H_3C$$
  $SO_2$   $SO_2$   $C$   $SO_2$   $C$ 

$$H_5C_2$$
 $SO_2$ 
 $SO_2$ 
 $SO_3$ 
 $SO_3$ 

$$so_2-so_2$$
 $(\times \mathbb{I} - 6)$ 

$$H_5C_2O$$
 $SO_2-SO_2$ 
 $(XI - 7)$ 

## [0076]

## [Formula 51]

$$SO_2-SO_2$$
 OCH

## [0077]

### [Formula 52]

$$CI$$
  $SO_2$   $SO_2$   $OCH_3$ 

$$H_3C$$
 $H_3C$ 
 $(X II - 1 2)$ 

## [0078]

[Formula 53]

$$N-0-so_2$$
 $(X III -1)$ 

$$N-0-SO_2$$
 $CH_3$ 
 $(\times \mathbb{II} -2)$ 

$$N-0-SO_2$$
 OCH.

## [0079]

[Formula 54]

## [0800]

[Formula 55]

$$N-O-SO_2-OCH_3$$

$$N-0-SO_2-C_2H_5$$

$$0 \quad (\times \mathbb{II} \quad -7)$$

$$N-0-SO_2$$
 $(\times \mathbb{I} - 8)$ 

#### [0081]

#### [Formula 56]

$$N-O-SO_2-C_2H_5$$
  
 $O(\times III -10)$ 

$$\begin{array}{c} O \\ N-O-SO_2 + CH_2 \\ \hline \\ O \\ (\times \mathbb{II} -11) \end{array}$$

$$\begin{array}{c|c}
0 \\
N-0-SO_2
\end{array}$$

$$\begin{array}{c|c}
0 \\
(X III -12)
\end{array}$$

[0082] The addition of the compound which decomposes by the exposure of these activity beams of light or a radiation, and generates an acid is usually used in 0.001-40% of the weight of the range on the basis of the total solids of a photosensitive constituent, and is preferably used in 0.1-20% of the weight of the range. [0083] Well-known various compounds can be used for the positive type photosensitivity constituent of this invention if needed for the compound (sensitizer) which increases the photo-oxide generating effectiveness of the compound which generates said acid, a color, a pigment, a plasticizer, and the purpose that adjusts the solubility to the alkali water solution of a positive type photosensitivity constituent further. As a sensitizer, although electron-donative compounds, such as a pyrene and perylene, or merocyanine coloring matter, cyanine dye, etc. can be used, it is not limited to these. The range of the rate of these sensitizers and said components (b) is 0.1/1-5/1 in 0.01/1-20/1, and a weight ratio preferably at a mole ratio. Moreover, although a color can be used for the positive type photosensitivity constituent of this

invention as a coloring agent, there is an oil color or basic dye as a suitable color. Specifically, oil yellow #101, oil yellow #130, oil pink #312, the oil green BG, oil blue BOS, oil black BY, oil black BS, oil black T-505 (above product made from Oriental Chemical industry), a crystal violet (CI42555), Methyl Violet (CI42535), rhodamine B (CI45170B), Malachite Green (CI42000), a methylene blue (CI52015), etc. can be mentioned.

[0084] These colors can be preferably added in a photosensitive constituent at 0.1 -3% of the weight of a rate 0.01 to 10% of the weight to the total solids of a photosensitive constituent. Moreover, the filler of a cyclic anhydride and others etc. can be added as a compound which adjusts the solubility to the alkali water solution of the positive type photosensitivity constituent of this invention. There are phthalic anhydride [ which is indicated by the U.S. Pat. No. 4,115,128 specification as a cyclic anhydride ], tetrahydro phthalic anhydride, hexahydro phthalic anhydride, 3, and 6and oxy--tetrahydro phthalic anhydride, tetra-chloro phthalic anhydride, a maleic anhydride, a chloro maleic anhydride, alpha-phenyl maleic anhydride, a succinic anhydride, pyromellitic acid, etc. Sensibility can be raised to a maximum of 3 about times by making these cyclic anhydrides contain one to 15% of the weight to the total solids of a photosensitive constituent preferably. It is the purpose which takes out the soluble difference of the exposure section and an unexposed part. Furthermore, for example, JP,62-27829,A, JP,63-250642,A, JP,63-139343,A, Japanese Patent Application No. No. 177031 [two to], Japanese Patent Application No. No. 1381150 [ two to ], Japanese Patent Application No. No. 181151 [ two to ], Japanese Patent Application No. No. 45439 [ 59 to ], JP,63-139343,A, JP,48-39003,A, JP,51-120714,A, An official report or specifications, such as JP,53-133429,A, JP,55-126236,A, JP,1-106038,A, and JP,64-57258,A, hydrolyze with the acid of a publication, and the compound used as alkali soluble can be used.

[0085] The positive type photosensitivity constituent of this invention is melted to the solvent which dissolves each above-mentioned component, when using it as an ingredient for the lithography versions, and it is applied on a base material. Moreover, it is used as objects for resist ingredients, such as a semi-conductor, dissolving in a solvent. As a solvent used here, ethylene dichloride, a cyclohexanone, A methyl ethyl ketone, a methanol, ethanol, propanol, ethylene glycol monomethyl ether, 1-methoxy-2-propanol, ethylene glycol monoethyl ether, 2-methoxy ethyl acetate,

1-methoxy-2-propyl acetate, Dimethoxyethane, methyl lactate, ethyl lactate, N,N-dimethylacetamide, there are N.N-dimethylformamide, tetramethyl urea, N-methyl pyrrolidone, dimethyl sulfoxide, a sulfolane, gamma-butyl lactone, toluene,

ethyl acetate, dioxane, etc., and independent in these solvents — or it is mixed and used. The concentration of the above-mentioned component in a solvent (total solids containing an additive) is 2 – 50 % of the weight preferably. Speaking of 0.5 – 3.0 g/m2 and a photoresist, generally, 0.1 – 3.0 g/m2 is moreover, desirable [generally], for example speaking of the photosensitive lithography version, although coverage changes with applications when using it, applying as solid content as solid content. Although photosensitivity becomes size as coverage decreases, the coat property of a film falls.

[0086] When manufacturing the lithography version using the positive type photosensitivity constituent of this invention, as the base material for example, paper and plastics (for example, polyethylene and polypropylene --) The paper which polystyrene etc. laminated, for example, aluminum, (an aluminium alloy is also included) Metal plates, for example, diacetyl cellulose, such as zinc and copper, a cellulose triacetate, Cellulose propionate, a butanoic acid cellulose, a cellulose acetate butyrate, a cellulose nitrate, Polyethylene terephthalate, polyethylene, polystyrene, polypropylene, The film of plastics, such as a polycarbonate and a polyvinyl acetal, the paper in which the metal like the above was laminated or vapor-deposited, or plastic film is contained. Among these base materials, the aluminum plate is remarkably stable in dimension, and especially since it is moreover cheap, it is desirable. Furthermore, the complex sheet with which the aluminium sheet was combined on a polyethylene terephthalate film which is being described at JP,48-18327,B is also desirable. The brush graining which carries out nylon brush surface roughening of the front face of an aluminum plate while pouring out the slurry of wye YABURASHIN graining and a polish particle, The mechanical approaches, such as ball graining, graining by liquid honing, and buff graining, HF, and AlCl3 and HCl Chemical graining made into etchant, After graining a front face by the compound graining performed by compounding the electrolysis graining which uses a nitric acid or a hydrochloric acid as the electrolytic solution, and these surface roughening methods, What etching processing was carried out with an acid or alkali if needed, anodized in a direct current or AC power supply succeedingly in a sulfuric acid, a phosphoric acid, a chromic acid, sulfamic acid, or these mixed acids, and prepared the firm passive state coat in the aluminum front face is desirable. Moreover, what performed sealing is desirable after graining processing and anodic oxidation. This sealing is performed in the immersion list to hydrothermal solusion including hot water and mineral salt, or organic salt by the steam bath etc. [0087] Although hydrophilization of the aluminum front face is carried out by the passive state coat itself [ such ] furthermore, the silicate processing (a specific

silicate --) indicated by the U.S. Pat. No. 2,714,066 specification and the U.S. Pat. No. 3,181,461 specification if needed A potassium silicate, the fluoride zirconic acid potassium processing indicated by the U.S. Pat. No. 2,946,638 specification, The phospho MORIBU date processing indicated by the U.S. Pat. No. 3,201,247 specification, The alkyl titanate processing indicated by the British JP,1,108,559,B specification, Germany patent 1,091,443rd Polyacrylic acid processing indicated by the number specification, Germany patent 1,134,093rd A number specification and British patent 1,230,447th Polyvinyl phosphonic acid processing indicated by the number specification, The phosphonic acid processing indicated by JP,44-6409,B, the phytic acid processing indicated by the U.S. Pat. No. 3,307,951 specification, At \*\* to the complex of the hydrophilic organic high molecular compound indicated by each official report of JP,58-16893,A or JP,58-16291,A, and a divalent metal ion Undercoat processing, Especially the thing that performed hydrophilization processing by the undercoat of the water-soluble polymer which has the sulfonic group indicated by JP,59-101651,A is desirable. As other hydrophilization arts, the silicate electrodeposition indicated by the U.S. Pat. No. 3,658,662 specification can be mentioned.

[0088] The positive type photosensitivity constituent of this invention is applied on the above-mentioned base material by the well-known spreading technique. As an example of the above-mentioned spreading technique, the rotation applying method, the wire bar applying method, the DIP applying method, the Ayr knife applying method, a roll coating method, the blade applying method, the curtain applying method, a spray coating cloth method, etc. can be mentioned. The layer of the positive type photosensitivity constituent applied as mentioned above is dried for [ 30 seconds - ] 10 minutes using hot air drying equipment, a ultrared ray dryer, etc. at 40-150 degrees C. The approach of applying heat after the approach bridge formation with a component (a) and a component (b) applies heat at the time of spreading of a photosensitive constituent and desiccation, or spreading desiccation etc. is mentioned. Heating is 80 degrees C or more still more preferably, and is performed 2 minutes or more preferably 30 seconds or more 60 degrees C or more. When using the positive type photosensitivity constituent of this invention as a photoresist, the substrate of the various quality of the materials, such as a copper plate or a coppering plate, a silicon plate, a stainless plate, and a glass plate, can be used as a base material.

[0089] Image exposure and a development process are usually given to the photosensitive lithography version or a photoresist containing the positive type

photosensitivity constituent of this invention etc. As the light source of the activity beam of light used for image exposure, there are a mercury-vapor lamp, a metal halide lamp, a xenon lamp, a chemical lamp, a carbon arc lamp, etc., for example. As a radiation, there are an electron ray, an X-ray, an ion beam, far ultraviolet rays, etc. As the light source for photoresists, g line, i line, and Deep-UV light are used preferably. Moreover, the scan exposure by the high density energy beam (a laser beam or electron ray) can also be used for this invention. As such a laser beam, a helium neon laser, an argon laser, krypton ion laser, a helium cadmium laser, a KrF excimer laser, etc. are mentioned. As a developer used for the development of the positive type photosensitivity constituent of this invention, the water solution of inorganic alkali chemicals, such as a specific silicate, a potassium silicate, a sodium hydroxide, a potassium hydroxide, a lithium hydroxide, the third sodium phosphate, sodium diphosphate, the third ammonium phosphate, dibasic calcium phosphate, specific metasilicate, sodium bicarbonate, and aqueous ammonia, and organic alkali chemicals, such as a tetra-alkylammonium hydride, is suitable, and 0.1 to 10% of the weight, those concentration is added so that it may become 0.5 - 5% of the weight preferably. Moreover, organic solvents, such as a surfactant and alcohol, can also be added to this alkaline water solution if needed.

#### [0090]

[Effect of the Invention] The positive type photosensitivity constituent of this invention has high photosensitivity, and use of a wide range wavelength light is possible for it.

#### [0091]

[Example] Hereafter, although an example explains this invention to a detail further, thereby, the contents of this invention are not limited.

After having been immersed in 10% water solution of the sodium tertiary phosphate which kept 2S aluminum plate with examples 1–24, an example [ of a comparison / 1 ] – a 3 thickness of 0.24mm at 80 degrees C for 3 minutes, degreasing and graining with a nylon brush, it etched for about 10 minutes by the sodium aluminate, and 3% water solution of sodium hydrogensulfates performed the desmut treatment. It is this aluminum plate in 20% sulfuric acid Current density 2 A/dm2 It set and anodic oxidation was performed for 2 minutes. 27 kinds of sensitization [liquid A]-1-[A]-24 and [A']-1-[A']-3 were prepared using the compound shown in the next following table 1 as the following formula. It applied on the aluminum plate which anodized this sensitization liquid, it dried for 10 minutes at 100 degrees C, and each photosensitive lithography version was created. All the coverage at this time was adjusted so that it

might become 1.7 g/m2 with dry weight.

The linear macromolecule of the sensitization liquid formula [A] table 1 The vinyl ether compound of the 2.0g table 1 The photo-oxide generating agent of the 0.4g table 1 0.1g dioxane 50.0g methanol In order to check bridge formation of the sensitization layer by the heat at the time of 15.0g desiccation, after being immersed in the solvent shown in Table 2 for 5 minutes and rinsing the obtained photosensitive lithography version, the dissolution condition of a paint film was observed. The result is shown in Table 2. O The dissolution and \*\* express the dissolution (film decrease) and x expresses non-\*\* in part. Next, the gray scale of the concentration difference 0.15 were stuck on the sensitization layer of the obtained photosensitive lithography version, and the 2kW high pressure mercury vapor lamp performed exposure for 20 seconds from the distance of 50cm. The developer undiluted solution of the following presentations after heating the exposed photosensitive lithography version at 120 degrees C for 5 minutes (Y): Water 80g triethanolamine 3gt(s)-butyl naphthalene sulfonic-acid sodium 8g benzyl alcohol When it was immersed for 60 seconds and negatives were developed in 25 degrees C in the 9g two-fold-serial-dilution water solution, as for all the photosensitive constituents of this invention, the clear positive image was obtained. A result is shown in Table 3.

[0092]

#### [Table 1]

Table 1 Sensitization liquid Line \*\* Quantity Part Child BINIRUE Photo-oxide generating agent The Tell compound Example 1 [A] -1 A methacrylic acid / 2-hydroxy II-11 X-21 Ethyl methacrylate/meta Krill acid methyl =20/20/60 (% of the weight) molecular weight Mw=2.8 10,002 2 methacrylic acids / 2-hydroxy II-11 X-21 Ethyl methacrylate/meta Krill acid methyl =30/10/60 (% of the weight), molecular weight Mw= 29,000 3 3 A methacrylic acid / 2-hydroxy II-11 X-21 Ethyl methacrylate / methyl-methacrylate =35/5/60 (% of the weight) Molecular weight Mw = [ 27,004 ] 4 An acrylic acid / 2-hydronalium KISHIE II-11 X-21 Benzo[ chill methacrylate / ] RUMETA chestnut rate =20/20/60 (% of the weight) molecular weight Mw= 32,000 5 5 An acrylic acid / 2-hydronalium KISHIE II-11 X-21 Benzo[ chill methacrylate / ] RUMETA chestnut rate =30/10/60 (% of the weight) molecular weight Mw= 29,000 6 6 An acrylic acid / 2-hydronalium KISHIE II-11 X-21 Chill methacrylate / benzyl methacrylate =35/5/60 (% of the weight), molecular weight Mw= 35,000 7 7 A methacrylic acid / 2-hydroxy II-11 X-21 Ethyl methacrylate/Ben JIRUMETA chestnut rate =20/20/60 (% of the weight) molecular weight Mw= 42,000 8 8 itaconic acids /p - (2-hydronalium KISHIE) [ II-11 X-21] Chill styrene / methyl-acrylate

=15/20/65 (% of the weight), Molecular weight Mw= 42,000 9 9 A maleic acid / p-hydronalium KISHISUCHI II-11 X-21 Wren / ethyl-acrylate = 15/50/35 (% of the weight), molecular weight Mw = 32,000 10 10 Acrylic resin "[ KARUBO set XL II-11 ] X-21 - 44" good rich company make 11 11 Acrylic resin "KARUBO set II-11 X-21 525" good rich company make 12 12 Acrylic resin "KARUBO set II-11 X-21526" good rich company make 13 13 A methacrylic acid / 2-hydroxy II-9 X-21 Ethyl methacrylate/Ben JIRUMETA chestnut rate =20/20/60 (% of the weight) Molecular weight Mw= 42,000 1414 A methacrylic acid / 2-hydroxy II-35 X-21 Ethyl methacrylate/Ben JIRUMETA chestnut rate =20/20/60 (% of the weight) molecular weight Mw= 42,000 15 15 A methacrylic acid / 2-hydroxy VII-9 XI-32 Ethyl methacrylate/Ben JIRUMETA chestnut rate =20/20/60 (% of the weight) molecular weight Mw= 42,000 16 16 A methacrylic acid / 2-HIDOROKI VII-11 X-21 SHIECHIRU methacrylate / Ben JIRUMETA chestnut rate =20/20/60 (% of the weight) molecular weight Mw= 42,000 17 17 Same as the above VII-3 X-22 18 18 Same as the above VII-6 X-22 19 19 Same as the above VII-13VIII-3 20 20 Same as the above II-11 X-2221 21 Same as the above II-11 IX-8 22 22 Same as the above II-4 XII-10 23 23 same as the above II-17 XIII-12 24 24 A methacrylic acid / benzyl meta II-11 X-21 Chestnut rate =20 / 80 (% of the weight) molecular weight 28,000 and 1g -- and A methacrylic acid / 2-hydronalium KISHIE chill methacrylate = 50/50 (% of the weight) Molecular weight 22,000, 1g Example 1 of a comparison [A'] -1 A methacrylic acid / 2-hydroxy II-11 Nothing Ethyl methacrylate/Ben JIRUMETA chestnut rate =20/20/60 (% of the weight) molecular weight Mw= 42,000 2 2 A methacrylic acid / methyl METAKU II-11 X-21 RIRETO = [ 40/60 (% of the weight), ] Molecular weight Mw= 32,000 3 32-hydroxyethyl meta-chestnut II-12 X-21 Rate/Benzyl meta-KURIRE - TO = 20/80 (% of the weight) Molecular weight Mw= 43,000 [0093] [Table 2]

Table 2 Solubility of dry paint film Y/water (1/2) Methyl ethyl ketone Dioxane Toluene Example 1  $\times$  x  $\times$  x 2  $\times$  x  $\times$  x 3  $\times$  x  $\times$  x 4  $\times$  x  $\times$  5  $\times$  x  $\times$  6  $\times$  x  $\times$  7  $\times$  x  $\times$  x eight x  $\times$  x 9  $\times$  x x ten xx  $\times$  11  $\times$  x  $\times$  12  $\times$  x  $\times$  13  $\times$  x  $\times$  14  $\times$  x  $\times$  15  $\times$  x  $\times$  16  $\times$  x  $\times$  17  $\times$  x  $\times$  18  $\times$  x  $\times$  19  $\times$  x  $\times$  20  $\times$  x  $\times$  21  $\times$  x  $\times$  22  $\times$  x  $\times$  23  $\times$  x  $\times$  24  $\times$  x  $\times$  Example 1 of a comparison x  $\times$  x  $\times$  2 O O O \*\* 3  $\times$  O O \*\* [0094]

[Table 3]

Table 3 The image engine performance Number of stages of gray scale Example 1 A clear positive image 10 2 A clear positive image 9 3 A clear positive image 8 4 A clear positive image 11 5 Clear positive image 11 6 A clear positive image 10 7 A clear positive image 12 8 Clear positive image 12 9 A clear positive image 12 10 Clear

positive image 10 11 A clear positive image 812 A clear positive image 9 13 Clear positive image 9 14 A clear positive image 10 15 A clear positive image 1016 A clear positive image 4 17 — clear positive image Seven 18 Clear positive image 6 19 — clear positive image Four 20 Clear positive image 13 21 A clear positive image 2 22 Clear positive image 523 A clear positive image 7 24 Clear positive image 3 Example 1 of a comparison The exposure section and an unexposed part are insoluble. 2 The exposure section and an unexposed part are film decrease (with no image).

[0095] Apply sensitization [liquid A]-1, [A]-4, [A]-7, and [A]-16 with a spinner on a silicone wafer with an example [ 25 ] - a 28 thickness of 2mm, it is made to dry for 2 minutes at 120 degrees C, and the thickness at the time of desiccation is 1 g/m2. It adjusted so that it might become. The obtained resist was exposed using the contraction projection aligner (stepper) using the homogeneous light with a wavelength of 436nm, and it heated for 3 minutes at 120 degrees C after that. The resist pattern was made to form by developing negatives for 60 seconds in 2.4% water solution of tetramethylammonium hydroxide. Consequently, in all samples, the good pattern of a 0.7-micrometer Rhine and a tooth space was obtained.

The gray scale of the concentration difference 0.15 were stuck for the photosensitive lithography version obtained in the example 29 example 17 on the sensitization layer, and the 2kW high pressure mercury vapor lamp performed exposure for 20 seconds from the distance of 50cm. After heating the exposed photosensitive lithography version at 120 degrees C for 5 minutes, in 25 degrees C, 20 seconds, 30 seconds, 1 minute, 2 minutes, 5 minutes, 10 minutes, and developing time were changed and developed in the two-fold-serial-dilution water solution of Y-3C (trade name: Fuji Photo Film make). Consequently, the good positive image was obtained in all and all gray scale number of stageses were 13 steps. By the above result, the positive type photosensitivity constituent of this invention is high sensitivity, and the clear positive image was obtained. Moreover, the example 29 showed that the development latitude of a positive type photosensitivity constituent was large.

[Translation done.]